

Detection and Characterization of Surface-Active Material in the Marine Atmosphere

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ABSTRACT

Organic constituents of the marine atmosphere were collected on shallow trays exposed to onshore winds on the windward coast of the Island of Oahu. Upon addition of distilled water to the trays the collected materials formed monomolecular films on the water surface, and film pressure-vs-area curves for these films were determined at the field site. The monolayer studies indicated the presence of weakly surface-active organic compounds and hydrocarbons, as well as strongly adsorbed, highly polar species. Simultaneous collections of oceanic particulate matter were made with a high-volume air sampler using glass fiber filters. The organic material was extracted from the filters with chloroform and analyzed for specific fatty acids by gas chromatography. The ratios of the quantities of the principal fatty acids found in the air samples were similar to previously reported fatty acid ratios from sea surface samples which had been collected at the air/sea interface. It was concluded that the ocean appears to be a major source of airborne maritime organic matter. The implications of these data to sea fog and haze stabilization are discussed.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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DETECTION AND CHARACTERIZATION OF SURFACE ACTIVE MATERIAL IN THE MARINE ATMOSPHERE

INTRODUCTION

The role of organic surface-active substances in the modification of atmospheric processes has received little scientific attention and presently remains unresolved. However, some research has suggested that surface films may influence the growth and stability of clouds and fogs. Certain organic monomolecular films decrease the evaporation rate of small drops (1) as well as retard the growth rate of film-covered saline drops at low levels of water vapor supersaturation (2). Evaporation retardation becomes significant when the linear molecules of the organic film become closely packed on a shrinking droplet surface. Since a natural organic film would concentrate at the surface of an evaporating drop, Goetz (3) has suggested that this process might stabilize sea fogs at low humidities, creating a rather permanent haze of high organic content.

A mechanism for the transport of organics from the sea into the marine atmosphere was described by Blanchard (4) who demonstrated that organic surface-active materials were ejected into the atmosphere on fragments from bursting bubbles and also showed the presence of this material in marine air (5). An air bubble in the sea is an active adsorber and a vehicle for the transport of organic material to the air/sea interface (6). Rupture of the bubble at the sea surface continues the transport of the organic from the sea into the air, ejecting not only the ocean surface constituents but also surface-active substances that were adsorbed onto the bubble during its rise through the organic-rich upper segment of the sea.

At present there is little evidence to relate organic material of the marine atmosphere to its source, whether it be oceanic, continental, or man-made. Furthermore, there is almost no information on the chemical composition of the organic constituents of the ocean atmosphere. Therefore, the goals of this investigation were to collect material from the marine atmosphere, to measure surface chemical properties of the material, and to identify some of the specific compounds and classes of chemicals present. From such information the source of the airborne material may be determined, and the possibility of fog stabilization by naturally occurring surface-active material may be judged.

COLLECTION SITE

An island with a continuous onshore wind provides the most suitable collection site for long-period sampling of organics in the marine atmosphere. Samples collected from an onshore wind with a long oceanic fetch are not affected by the organic combustion products normally encountered aboard ship or by continental air pollution. For this reason the air sampling program was conducted on the north side of the eastern tip of the Island of Oahu at the collection station maintained by the Hawaiian Institute of Geophysics. With the exception of one day, there was a continuous onshore wind during the sampling period from May 1 to May 15, 1969. The collection devices were mounted at the top of the station's 20-m-high tower located about 20 m from the water's edge. The elevation prevented collection of spray from the surf zone which is rich in both sea salt and organic ingredients.

HIGH-VOLUME AIR SAMPLING AND ISOLATION OF ORGANIC CONSTITUENTS

A high-volume air sampler using 8 in. x 10 in. Reeve Angel grade 934AH glass fiber filters was mounted at the top of the tower and operated at a rate of 60 cu ft/min. Before exposure, the glass fiber filters had been washed with chloroform, dried at 100°C overnight, weighed, and individually heat-sealed in polyethylene bags. The filters were unpacked at the tower top just prior to insertion into the high-volume air sampler. At all times the filters were handled only with tongs. At the conclusion of a sampling period the filter was removed from the air sampler, placed directly into its original polyethylene bag, and resealed. The sampler was operated continuously for 8 hr during each of the first four collections and for 24 hr during each subsequent collection.

In the laboratory each filter was unpackaged and weighed to determine by difference the total quantity of material collected. The filter was immediately placed in a Soxhlet extractor and extracted for 4 hr with 150 ml of chloroform which had been freshly distilled into the Soxhlet apparatus through a Vigreux column. The extract was concentrated by distilling off chloroform until the volume had decreased to about 40 ml. The sample was then poured through a freshly rinsed, glass fiber filter into a previously weighed 60-ml glass-stoppered bottle. Chloroform distilled from the concentrated sample was used to rinse the filter before pouring the sample through. Air filtered through a firmly packed cotton column was used to evaporate the remaining chloroform from the organic constituents of the sample.

The total amount of material collected was determined by weighing each glass fiber filter before and after sampling. These values are reported in Table 1 as "total salt." The total quantity of material extracted from each filter by 150 ml of chloroform was corrected for a blank of 2.4 mg and reported in the same table as "organics extracted by CHCl_3 ." The organics made up from 5% to 15% of the airborne particulate matter that was collected. The blank was due to tiny glass fibers from the filters which became suspended in the chloroform during the extraction process. A small quantity of these particles passed into the evaporating bottle and could be identified by a low-power microscope when collected on a 0.3-micron millipore filter. A concentrated blank sample was centrifuged to remove the fibers. The remaining chloroform left no detectable residue after evaporation.

Nine of the extracted samples were redissolved in chloroform and combined into four samples of approximately 10 mg each. These were evaporated to dryness and sent to Florida State University for analyses by gas chromatography. The samples were treated with BF_3 :methanol using the conditions described by Morrison and Smith (7), and the methyl esters were extracted with hexane. The concentrated hexane extract was then analyzed at column temperatures of 130 and 160°C. Each analysis was performed at least twice. The F&M Model 700 gas chromatograph was equipped with dual 4-ft glass columns packed with 10% diethylene glycol succinate on 100/120 mesh gas chrom Q. Compounds were identified only by their retention times.

The chromatograms contained a number of peaks, and substances with retention times corresponding to the five standards were detected (Fig. 1). The relative areas were determined by using the height times the width at half height. The five identified peaks accounted for more than two-thirds of the material indicated by the spectra. However, based on the weights of the samples submitted for analysis and on the calibration of the instrument, less than 5% of the material in each sample consisted of a mixture of the five identified fatty acids. The relative proportions of the five fatty acids were determined from ratios of their peak areas to that of palmitic acid. Such ratios were obtained for each sample and averaged to give an overall ratio for all samples collected. Chromatographic data on naturally occurring surface films collected from various ocean

Table 1
Atmospheric Sampling Data

| Sample No. | Total Salt (mg) | Organics Extracted by CHCl_3 (mg) | Volume Sampled (m^3) | Salt ($\mu\text{g}/\text{m}^3$) | Organics ($\mu\text{g}/\text{m}^3$) | Average Wind Speed (m/sec) |
|------------|-----------------|--|---------------------------------|-----------------------------------|---------------------------------------|----------------------------|
| 1 | — | 3.9 | 903 | — | 4.3 | 7.9 |
| 2 | 37 | 4.8 | 758 | 49 | 6.3 | 8.5 |
| 3 | 35 | 3.0 | 864 | 41 | 3.5 | 8.3 |
| 4 | 27 | 3.8 | 800 | 34 | 4.8 | 7.5 |
| 5 | 64 | 7.9 | 2429 | 26 | 3.3 | 7.1 |
| 6 | 61 | 6.3 | 2424 | 25 | 2.6 | 4.1 |
| 7 | 44 | 3.7 | 2439 | 18 | 1.5 | 1.5 |
| 8 | 27 | 2.1 | 2263 | 12 | 0.9 | 2.2 |
| 9 | 26 | 1.9 | 2693 | 10 | 0.7 | 3.3 |
| 10 | 43 | 3.1 | 4432 | 10 | 0.7 | 1.5 |
| 11 | 56 | 2.5 | 2492 | 23 | 1.0 | 1.0 |
| 12 | 54 | 4.3 | 2410 | 22 | 1.8 | 2.6 |
| 13 | 41 | — | 2334 | 18 | — | 3.9 |

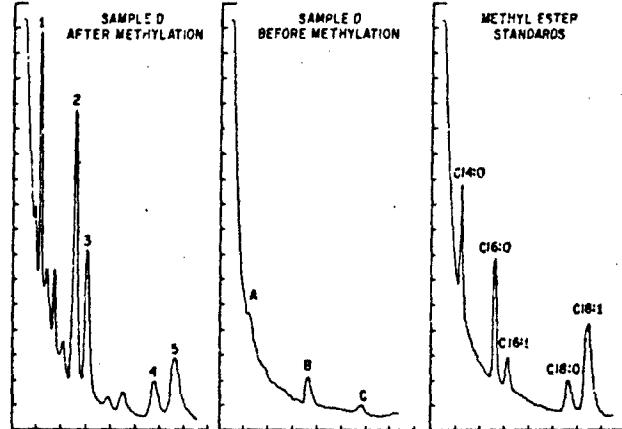


Fig. 1 - Gas chromatogram for organic material extracted from glass fiber filters

locations has been reported by Garrett (8). Sufficient data were reported for thirteen of the sea surface samples to permit the calculation of the relative proportions of the same five fatty acids. The averages of the ratios of the acids to palmitic acid were compared to the averages from the marine air collections (Table 2). There was a strong correspondence between the relative quantities of fatty acids in the sea and air samples, with only the octadecanoic acid (C 18:0) values differing significantly. Although these results may be fortuitous, they suggest that much of the organic load of the marine atmosphere is of oceanic origin.

Table 2
Ratios of Fatty Acids to Palmitic Acid

| Fatty Acids | C 14:0 | C 16:0 | C 16:1 | C 18:0 | C 18:1 |
|---|--------|--------|--------|--------|--------|
| Ratios in Air Samples | 0.4 : | 1.0 : | 0.5 : | 0.2 : | 0.5 |
| Ratios in Sea Surface Samples | 0.3 : | 1.0 : | 0.4 : | 0.7 : | 0.5 |
| (C18:1 = 18 carbon acid with 1 double bond) | | | | | |

The relationship of salt concentration and organic concentration to the average wind speed is depicted in Fig. 2. The straight lines were computed by the method of least squares applied to the wind speed and to the logarithm of the concentrations (Table 1). In general, the salt concentrations were only slightly higher than those measured by Woodcock (9), but at least an order of magnitude lower than the values reported by Jacobs (10) for air that was probably loaded heavily with salt by the surf. Thus the collected samples were representative of marine air that was free of surf zone influence. An interesting feature of Fig. 2 is the difference in the slopes of the two lines. Although more data would be required for confirmation, the difference suggests an increase in the ratio of organic material to total salt as wind speed increases. Such an effect may be due to an increase in the bubble bursting and spray activity with increasing wind speed. Both processes transport adsorbed surface-active substances from the sea into the marine atmosphere.

SURFACE CHEMICAL CHARACTERIZATION OF AIRBORNE ORGANIC MATERIAL

Surface chemical characteristics of airborne organic material were determined at the field site. Samples were collected on brass trays coated with paraffin wax that were exposed at a 45 degree angle to the onshore wind at the tower top. Each tray was divided into two triangular sections that were 77.5 cm \times 25.0 cm and 3 mm deep. After a 24-hr exposure period a tray was carried to the shed at the base of the tower where one section was filled with distilled water and allowed to stand for 15 min while the surface-active material adsorbed at the water surface. The adsorbed film was then slowly compressed into a smaller area by a paraffin-coated brass bar. Frequent surface tension measurements were made during the compression of the film. A duplicate set of measurements was made using the second half of the tray. Water used as a substrate was distilled three times with the second distillation from alkaline potassium permanganate. The paraffin-coated trays were cleaned of surface-active material between collections by rinsing thoroughly with distilled water and then allowing triply distilled water to stand in them for 30 min before discarding.

Surface tension measurements were made by the Wilhelmy plate method (11) using a 1 sq cm \times 0.005 cm thick platinum plate which was suspended from the microscale accessory of a Statham Universal Transducing Cell (Model UC2). The apparatus was calibrated with standard platinum weights before each series of measurements. The transducing cell forms part of a Wheatstone bridge which becomes unbalanced when a small force strains one of the resistance elements. The cell was coupled to a battery-powered portable

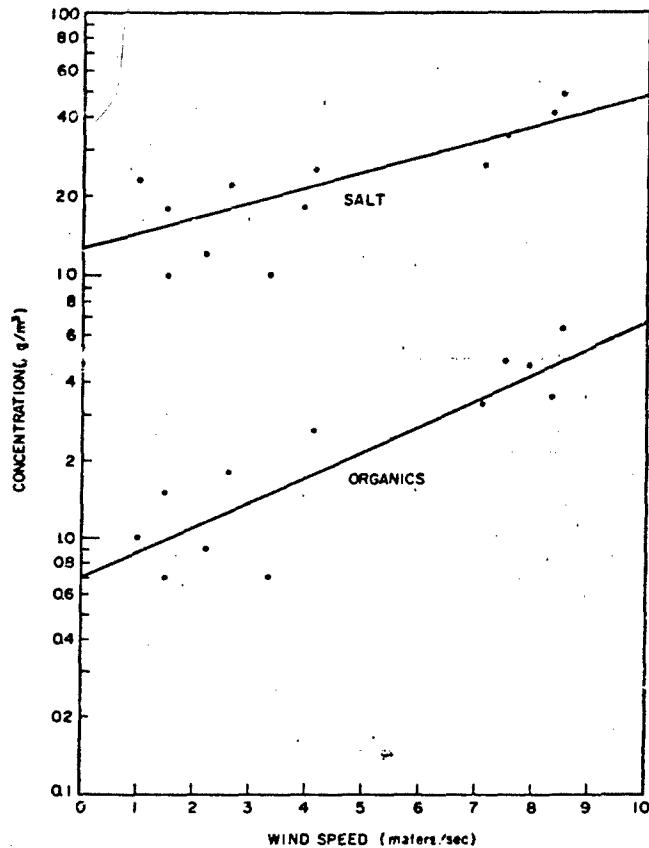


Fig. 2 - Concentration of sea salt and concentration of organics as a function of wind speed

millivolt potentiometer* through a bridge balancing unit. The circuit for the balancing unit is shown in Fig. 3. It can also be used with a sensitive chart recorder. When using a 1-cm plate a change in surface tension of 72 dynes/cm produces a change of approximately 2400 μ V. Readings can be estimated to the nearest microvolt with an accuracy of approximately $\pm 5 \mu$ V. This portable system gives excellent linear response to forces in the 0-to-1000-dyne range.

Typical results are presented in Fig. 4, where film pressure is shown as a function of the area occupied by film. Film pressure is the surface tension difference between clean water and water covered with adsorbed surface film. The curves shown are the averages of results from both sections of the tray corrected to a 24-hr exposure time by dividing the area values by the exposure time and multiplying by 24. All tray exposures were from 23 to 26 hr except for one which was for 4 hr. The F-vs-A (force-vs-area) curves were similar in shape to those reported from sea surface samples (12, 13). They

*This instrument has a range of 0-111 or 0-11.1 mV and is available from James G. Biddle Co., Plymouth Meeting, Pa.

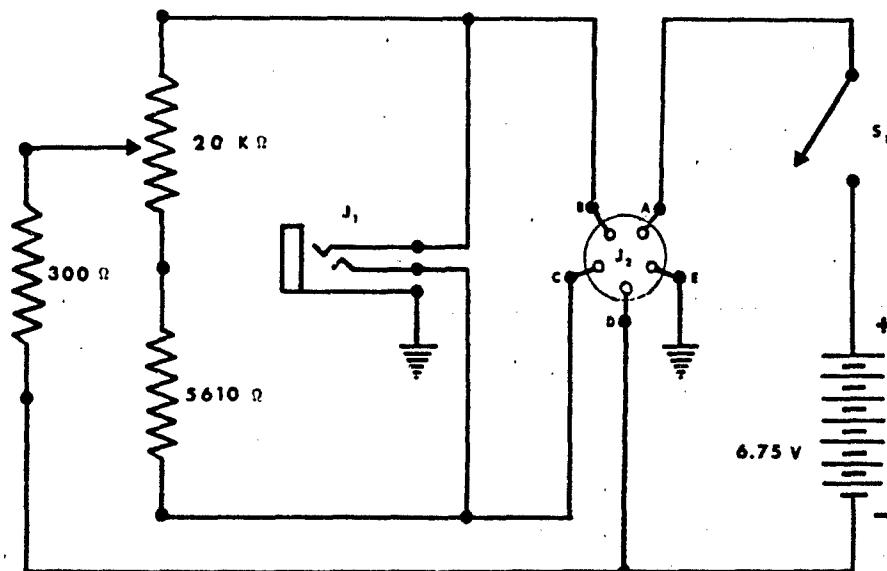


Fig. 3 - Circuit for the Wheatstone bridge balancing unit used with transducing cell and millivolt potentiometer. Potentiometer connects to J_1 ; transducing cell to J_2 . S_1 = on-off.

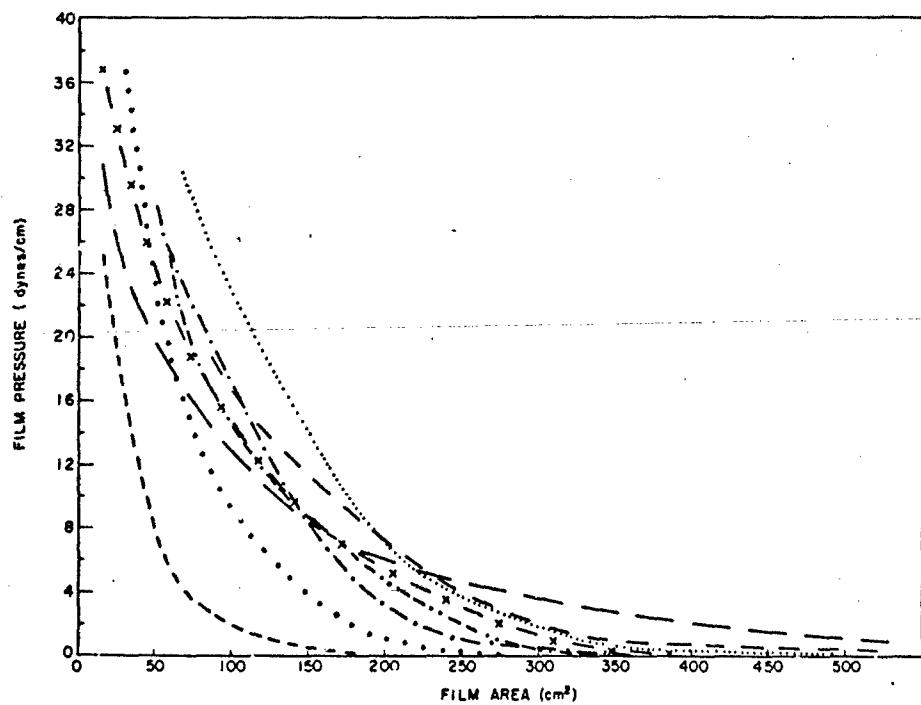


Fig. 4 - Film pressure vs area for films of surface-active material collected from marine air (24-hr tray exposures)

were of the liquid-expanded type and indicated the presence of unsaturated and weakly-surface-active compounds, and possibly nonpolar hydrocarbons. The F-vs-A curves were not reversible, i.e., repeated expansions and compressions of the same surface film indicated that substantial quantities of materials had been lost from the film by either solubilization into the substrate under pressure or irreversible collapse of the film. As a mixed film is compressed, competitive adsorption occurs and the remaining film becomes enriched with the most surface-active water-soluble species as the other compounds are displaced from the interface.

Mixtures of pure compounds were studied in the laboratory so that their chemical characteristics could be compared with those of the atmospheric organics. The study indicated that the shapes of the F-vs-A curves for the collected materials may be explained by the presence of (a) unsaturated compounds, (b) more soluble surface-active compounds of lower molecular weight, or (c) nonpolar hydrocarbons in addition to the fatty acids shown to be present. A mixture of all these is likely if the sea is a principal source of airborne organic material. Data for mixtures of pure palmitic acid (C 16:0) with paraffin oil, a nonpolar hydrocarbon mixture, are shown in Fig. 5 and provide some information about the curves due to naturally occurring airborne material. Variation in the area covered with the amount of pure surfactant spread is illustrated by the curves for 0.010, 0.030, and 0.050 mg of pure palmitic acid. Trays exposed for 24 hr seem to have collected a quantity of surface-active organics of the same order of magnitude. However, the collection efficiency of the trays is unknown, so the concentration in the air was not determined by this method. Pure paraffin oil gives no increase in film pressure with decreasing area when spread on distilled water; however, when only a trace of palmitic acid is dissolved in the paraffin oil, F-vs-area curves are produced that more closely resemble those for naturally occurring materials. With a mixture containing a wide variety of surface-active materials and nonpolar hydrocarbons, a more gradually sloping curve would be expected, such as those in Fig. 4. Therefore the shapes of the curves for airborne organic materials seem consistent with the gas chromatographic results which showed that the five identified strongly surfactant materials made up less than 5% of the total organic material collected.

CONCLUSIONS AND GEOCHEMICAL IMPLICATIONS

Experimental evidence from two independent collection and analytical procedures was obtained which demonstrated that material collected from the marine atmosphere contained a mixture of weakly-surface-active polar compounds, and possibly nonpolar hydrocarbons, as well as highly polar quite-surface-active species. Five fatty acids (C₁₄ - C₁₈) were specifically identified in relative proportions which were similar to their relative proportions in sea surface samples previously reported by Garrett (8). Surface chemical parameters (film pressure-vs-area curves) were measured on films formed by freshly collected organic fallout from ocean air without any intervening physical chemical handling. These plots were similar to F-vs-A data for natural organic surface films on seawater (12, 13).

The fact that transport mechanisms exist for the transfer of organic matter from the ocean across the air/sea interface and into the marine atmosphere, coupled with the chemical similarity between the sea surface material and the airborne organics, suggests that the sea is one of the principal sources of the organic constituents of maritime air. However, continental contributions to the total loading are certainly possible (14). Sampling at greater altitudes, along with more detailed chemical analyses for specific compounds, would be required to assess the extent of the continental input.

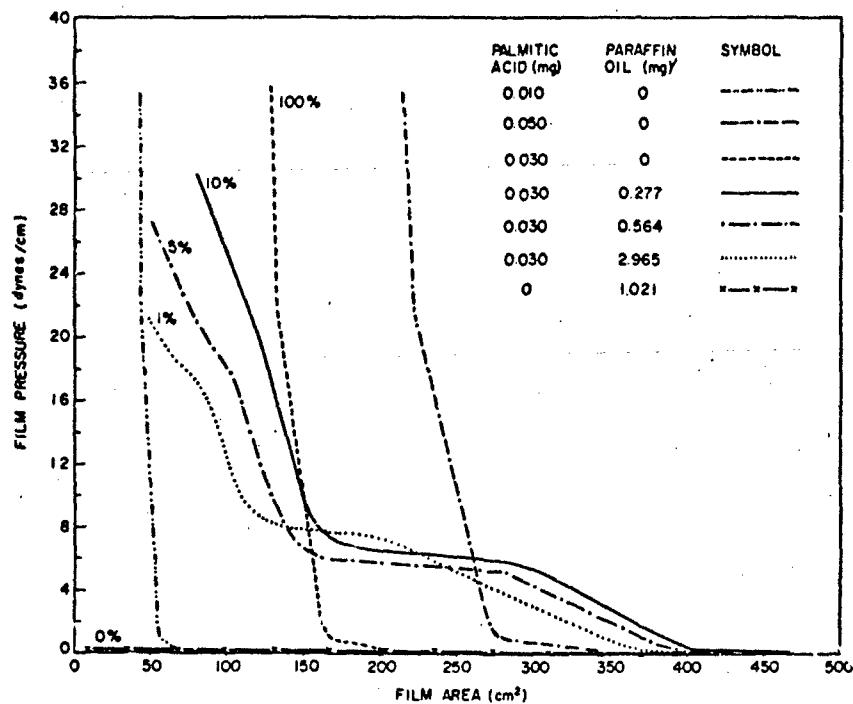


Fig. 5 - Film pressure vs area for films of known composition

The summary of gas chromatographic results (Table 2) is relevant to the idea that sea fogs and/or haze might be stabilized by surface-active films. The large body of literature dealing with evaporation retardation by monomolecular surface films composed of highly adlineated, straight chain fatty alcohols is cited as justification for this hypothesis. However, the effectiveness of such a film is greatly dependent upon the molecular geometry of its constituents. To retard the passage of water the molecules of the monolayer must be linear and capable of close packing in a condensed film. Permanently bent (chemically unsaturated) or branched hydrocarbon segments of the surface-active molecule, or ionization of the hydrophilic end group, prevents adlineation and reduces the ability of the monolayer to retard evaporation (15). The chemically unsaturated fatty acids detected in marine air (C 16:1 and C 18:1, Table 1.) comprised about 40% of the fatty acids determined. It was calculated that this quantity of unsaturated compounds would reduce the evaporation resistance of a straight chain fatty acid monolayer by 60%. An expression (16) for the evaporation resistance of a monolayer composed of two compounds with different evaporation resistances was used for the foregoing calculation. In addition, a monolayer with 1% of its area occupied by molecular holes (e.g., a hydrocarbon impurity, benzene) has its evaporation retardation efficiency reduced by 90-99% (17). The less polar compounds found in the marine air collections would essentially destroy the evaporation retardation characteristics of the linear fatty acid and fatty ester components of the surface film. Consequently, monomolecular films composed of the mixed surface-active material detected in marine air would not retard evaporation of spray or fog drops, although a small quantity of water might remain physically trapped by thick film segments of the remaining organic matrix.

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